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<b>(54) Title:</b> MODIFIED VISCOSE FIBRES AND METHOD FOR THEIR MANUFACTURE  <b>(57) Abstract</b>  The invention relates to a modified viscose fibres comprising viscose cellulose and containing in their structure microcrystalline chitosan forming after spinning mainly hydrogen bonds with the regenerated cellulose of viscose fibres. The microcrystalline chitosan contains chelated metal ions in order to modify and improve the properties of viscose fibres.		

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Modified viscose fibres and method for their manufacture

5 The present invention relates to modified viscose fibres and method for their manufacture.

10 Up to now chitosan containing viscose fibres and chitin/chitosan fibres have been manufactured using a viscose method. Chitin or chitosan is mercerized and reacted with carbon disulfide using a freezing stage at a temperature ranging from - 30 to 0°C. The freezing procedure has allowed to produce only chitin or chitosan derivatives able to dissolve in an aqueous sodium hydroxide solution and suitable for application as additives in the manufacture of modified viscose fibres or as a spinning dope for the production of polyaminosaccharide fibres.

20 The freezing procedure in the case of polyaminosaccharides has been favourable in improving their reactivity with carbon disulfide by a suitable change of the super-molecular structure of chitin/chitosan.

25 However, the preparation of polyaminosaccharide viscose must be realized in a rather long period, and the use of the freezing procedure in typical industrial conditions has caused several difficulties, which frequently make the production impossible for realization in practice.

30 Well-known methods for the production of the chitosan containing viscose fibres as well as polyaminosaccharide fibres production according to the viscose method are described among others in R.A.A. Muzzarelli's monography "Chitin", Pergamon Press, New York, 35 1977.

The well-known methods of polyaminosaccharide fibres production are based on the spinning of dissolved polymers into a regeneration bath or air.

- 5 Japanese Patent 81/112937 describes the production of chitosan fibres and films from an aqueous acid solution of chitosan. The spinning dope is filtered and spun through spinning nozzles and coagulated in an aqueous solution of anionic surfactants. Alternatively, the  
10 dope is sprayed on a smooth surface and then immersed into a coagulation bath to form a film.

- Japanese Patent 84/116418 discloses a production of chitosan fibres and films by dissolving chitosan  
15 into a solution of dichloroacetic acid in water. The solution is formed into fibres or films in aqueous solutions of metal salts and the formed product is treated with chelating metals.

- 20 Japanese Patent 81/106901 describes a method for a chitosan fibres production, based on chitosan and its salts molded from aqueous solutions using a basic gelation bath. Chitosan flakes are dispersed in water and heated with acetic acid at 40°C to give a dope  
25 containing 3% chitosan and 0.5% acetic acid. The dope is spun into a 5% aqueous sodium hydroxide solution at a temperature of 30°C, washed and dried to manufacture 3.5 denier fibres with tenacity of 2.44 G/denier, elongation of 10.8% and knot strength of 1.75 G/denier.

30

- European Patent Application EP 77.098 discloses a production of hollow chitosan fibres, useful for ultrafiltration and dialysis, with a diameter of 0.1  
35 - 1 mm and a thickness of 0.005 - 0.025 mm. The hollow fibres are produced by spinning the solution into an alkaline coagulant bath through hollow-fiber spinnerets using gaseous ammonia.

Japanese Patent 85/059123 describes the spinning of chitosan fibres by extruding solution of chitosan in an aqueous acetic acid and urea into an aqueous base and alcohol mixture. The acetic acid and urea content  
5 in the spinning solution are 0.5 to 20 wt% and 0.1 to 10 wt% respectively. The base bath is usually sodium hydroxide, potassium hydroxide or ammonium hydroxide used in a concentration of 1.0 to 50 wt%.

10 Japanese Patent 85/40224 describes the manufacture of chitosan fibres with improved tenacity and modulus. The fibres are prepared by spinning the aqueous acid solution of chitosan into air and by subsequently  
15 treating with gaseous ammonia and by washing, to obtain fibres with tenacity of 2 G/denier in a dry state, 0.82 G/denier in a wet state, elongation of 11% and modulus of 100 G/denier.

U.S. Patent 4,309,534 also describes a preparation  
20 of renatured chitosan fibres and films. The agitation of chitosan in the presence of aqueous solution of acetic acid, glycolic acid and pyruvic acid for 2-14 days at room temperature allows to produce fibres for use in the production of transparent films and  
25 birefringent fibres.

The microcrystalline chitosan and method for its manufacture are described in the Polish Patent 125995. The product according to this method is formed in a  
30 form of gel-like dispersion or powder. Microcrystalline chitosan shows raised reactivity and water retention value WRV of 200 - 500% in the powder form and WRV of 500 - 2000% in the gelatinous dispersion form, average molecular weight within a range of  $10^4$  -  $10^6$  and  
35 deacetylation degree not less than 30%.

The microcrystalline chitosan is characterized by the same chemical structure as the standard chitosan

raw material. However, it differs from this raw material by its super-molecular structure.

5 Finnish Patent 78126 describes the manufacture of chitosan-viscose fibres by introduction of an additive to a viscose dope, said additive being a microcrystal-  
line chitosan derivative obtained with carbon di-  
sulfide, the additive being added in a concentration  
10 of not less than 0.1 wt% on  $\alpha$ -cellulose weight, especially 0.5 - 25 wt%. The chitosan additive is produced by mercerization of microcrystalline chitosan in an alkaline solution, especially in an aqueous sodium hydroxide solution, whereafter the mercerized microcrystalline chitosan containing 1 - 10 wt% of  
15 polymer and 5 - 20 wt% of sodium hydroxide is reacted with carbon disulfide at a temperature not lower than 10°C for 1 - 120 minutes.

20 Finnish Patent 78127 discloses the manufacture of chitosan-viscose fibres using the microcrystalline chitosan as the additive to viscose dope in a concentration of not less than 0.01 wt%, especially 0.01 - 30 wt%, on the weight of  $\alpha$ -cellulose. The microcrystalline chitosan dispersion containing not  
25 less than 0.001 wt% of polymer is distributed into viscose, preferably by mixing for 1 - 60 minutes, and next the modified viscose is spun using standard conditions to obtain chitosan-viscose fibres characterized by super-absorbent and mild bacteriostatic  
30 behaviour as well as a better dyeability.

The well-known methods of manufacture of chitosan containing viscose fibres using a viscose method, as  
35 well as the methods of manufacture of polyaminosaccharide fibres require the use of several complicated operations and ingredients for the preparation of fibres.

The well-known chitosan containing viscose fibres are characterized by special properties as better dyeability especially by acid dyes.

- 5 The well-known polyaminosaccharide fibres are characterized by special mechanical properties, better dyeability, bacteriostatic action as well as biodegradability.
- 10 The chitosan-viscose fibres manufactured by addition of microcrystalline chitosan dispersion are characterized by only mild bacteriostatic behaviour as well as superabsorbent properties.
- 15 The object of this invention is to produce modified viscose fibres by direct application especially in a dispersion form of modified microcrystalline chitosan formed by chelating thereto active metal ions, to a viscose dope, the chitosan being introduced to the
- 20 viscose preferably by mixing or spurling into viscose dope before spinning, and/or by after-treating the modified viscose fibres by solutions of active metal ions chelatable to the chitosan within the viscose fibres.
- 25 According to the present invention, the modified viscose fibres contain in their structure microcrystalline chitosan chelated with metal ions having a synergistic effect on the chitosan bioactivity, such as copper,
- 30 zinc or calcium, the amount of the microcrystalline chitosan being not less than 0.01 wt%, especially 0.1 - 20 wt%, that of metal salts being 0.001 - 2 wt% and 60 - 90 wt% being  $\alpha$ -cellulose, the remainder being water and finishing agents.
- 35 According to the invention, the microcrystalline chitosan which is used for modification of viscose fibres, such as a dispersion preferably in water,

- characterized by a water retention value (WRV) in a dispersion form within a range of 500 - 2000% and 200 - 800% in a powder form, average molecular weight ranging from  $10^4$  to  $10^6$ , deacetylation degree not less than 30%, especially 60 - 90%, and content of polymer in dispersion not less than 0.01 wt%, preferably 0.5 - 5.0 wt%, is modified by chelating active metal ions such as copper, zinc or calcium in a molar ratio (glucosamine units/metal salts) not higher than 1:2, preferably 1:0.5 to 1:1, before introduction into a viscose dope, or alternatively in a molar ratio not lower than 1:0.1 in a case of aftertreatment of viscose fibres containing microcrystalline chitosan.
- 15 In accordance with a preferred embodiment of the method of the invention, the microcrystalline chitosan modified by chelating active metal ions such as copper, zinc or calcium, especially in a form of water dispersion, containing not less than 0.01 wt% of the microcrystalline polymer on a dry weight, especially 0.5-5.0 wt%, and metal ions chelated with the glucosamine units in molar ratio not higher than 1:2, is distributed into a viscose dope, preferably by mixing for a time within a range of 1 - 120 minutes, or
- 20 spurting before spinning, whereafter optionally the mixture is filtered and the spinning of modified viscose fibres is realized.
- 30 In accordance with a preferred embodiment of the method of the invention, the microcrystalline chitosan, especially in water dispersion, containing not less than 0.01 wt% of polymer, is modified by the chelating active metal ions by introduction of active metal salts, such as copper sulfate, zinc chloride or sulfate, or calcium chloride, in a form of a solid or
- 35 a solution into a microcrystalline chitosan dispersion in a molar ratio of glucosamine units to metal salts not higher than 1:2, preferably 1:0.5 to 1:1, using



mixing for 1 - 120 minutes at a temperature not lower than 10°C, preferably at a temperature ranging from 20° to 40°C.

5 In accordance with the invention, the introducing of modified microcrystalline chitosan with chelating active metal ions is realized by preparation of a concentrate of modified microcrystalline chitosan in viscose, containing 1 - 99.9 wt% of modified microcrystalline chitosan, the remainder being viscose, using a mixing or spurling system, especially for 1-60 minutes, whereafter the modified microcrystalline chitosan-viscose concentrate is introduced to a viscose dope by mixing or spurling and the modified viscose fibres are produced.

In accordance with the invention, modifying compounds, especially affecting the mixability, filtrability or improving the spinning process, such as polyethylene glycols, amines, polyamines, or ethoxylated phenols, in an amount not less than 0.01 wt% on the weight of  $\alpha$ -cellulose, are added to the modified microcrystalline chitosan and/or microcrystalline chitosan-viscose concentrate and/or viscose, and/or to modified viscose.

25 In accordance with a preferred embodiment of the method of the invention, the modified viscose fibres containing microcrystalline chitosan are subjected to an aftertreatment using the solutions of chelating active metal ions such as copper, zinc or calcium, in the form of copper sulfate, zinc chloride or sulfate, or calcium chloride, in a molar ratio of glucosamine units to metal salts not lower than 1:0,1, preferably 1:0.5 to 1:2, by mixing, washing or dipping of modified viscose fibres for a time ranging from 1 to 120 minutes at a temperature not lower than 10°C, especially 20-60°C.

- The microcrystalline chitosan used as a raw material for modification of viscose fibres is characterized by small aggregates with average dimension within a range of 0.01 - 100  $\mu\text{m}$ , this being the case especially in the dispersion form of microcrystalline chitosan. The aggregates are typically very flexible particles tending to disintegrate to individual particles under mechanical action or to deform their configuration under a suitable tension. The above advantages of microcrystalline chitosan, which are present also in the chelated form used in the invention, allow its use for direct modification of viscose fibres.
- Microcrystalline chitosan is characterized by a high ability to chelate several metal ions, based on its higher reactivity, higher intrinsic surface and larger capillary system in comparison to standard chitosan.
- The chelates of microcrystalline chitosan with active metal ions, such as copper, zinc or calcium, in a ratio suitable to combine the metal ions with the microcrystalline polymer, are characterized by the same technological properties as the initial material. The size distribution of particles of microcrystalline chitosan shows the percentage of particles having a dimension of 3.1 - 25  $\mu\text{m}$  of 93% of all particles, whereas the chelate of microcrystalline chitosan with calcium ions is characterized by a percentage of 81%, that with copper is 79.1%, and that with zinc is 75.8%. The modified microcrystalline chitosan in the form of a chelate with biologically active metal ions allows to introduce to viscose fibres the glucosamine polymer joined with the above-mentioned active metals, such as copper, zinc or calcium and others to improve the biological behaviour of viscose fibres. The introduction of several metal ions into the super-molecular structure of viscose fibres using the viscose

technology is possible only by the method according to the invention.

5 The main advantage of the modified viscose fibres according to the invention is concerned with the introduction of modified microcrystalline chitosan in the form of chelates directly to their structure without any changes in the chemical composition or main super-molecular structure of the microcrystalline  
10 chitosan chelate.

The modified viscose fibres contain in their structure the modified microcrystalline chitosan in the form of chelates with active metal ions, the chelated chitosan  
15 having been introduced directly to a viscose dope, or by aftertreatment of chitosan-viscose fibres with active metal ions the chitosan being thereafter dried together with the regenerated cellulose in the fibre structure.

20 Up to now there has not been known a direct introduction of chitosan chelates to the viscose dope and consequently to the structure of viscose fibres. All known methods are concerned with suitable changes of  
25 chitosan chemical structure to form suitable derivatives dissolved in the alkaline media or with a direct application of microcrystalline chitosan. The modified microcrystalline chitosan in a form of a suitable chelate, being a gel-like dispersion introduced into  
30 the structure of viscose fibres forms high energetic hydrogen bonds with the hydroxyl groups of the regenerated cellulose created in the viscose fibres.

A similar modified microcrystalline chitosan according  
35 to the invention is obtained in the structure of viscose fibres containing microcrystalline chitosan by a suitable aftertreatment using solutions of active metal ions.

The properties of modified microcrystalline chitosan affect the behaviour of modified viscose fibres, especially the sorption of water and dyes, mechanical properties, super-molecular properties as well as their bioactivity, especially bacteriostaticity.

The method of the manufacture of the modified fibres according to the invention is concerned with direct introduction of modified microcrystalline chitosan containing metal ions in a form of chelate into a viscose dope by simple systems of mixing or spurling for example, or by aftertreatment of viscose fibres containing microcrystalline chitosan in a wet or dry form in course of a finishing treatment by suitable solutions of metal salts. A benefit of modified microcrystalline chitosan, especially in a gel-like form, is related to its stability and excellent mixability with viscose in a wide range of concentration without any effect on the viscose stability.

The method according to the invention allows to introduce to a viscose dope the metal ions in a form of chelates joined with microcrystalline chitosan. These metal ions without an application of invented method would form undissolved derivatives with the viscose components as copper sulfite with a black colour for example, hence affecting the viscose dope properties and stability, or these salts would be completely washed out from the viscose fibres at the time of spinning and/or finishing treatment.

The modification of viscose fibres by modified microcrystalline chitosan in accordance with the invented method allows to obtain special viscose fibres in an industrial scale using standard viscose technology or standard aftertreatment methods at the finishing stage.

One of the advantages of the invented method is related to creation of a modified microcrystalline chitosan-viscose concentrate. The above-mentioned type of concentrate allows to improve the additive distribution in a viscose dope. A use of the modifying compounds in a method according to the invention, affecting the mixability, filtrability or improved spinning process, such as polyethylene glycols, amines, polyamines or ethoxylated phenols, added to the modified microcrystalline chitosan or viscose, facilitates the deformation of the gel-like dispersion particles of modified microcrystalline polymer at the time of distributing in a viscose or spinning.

The method in accordance with the invention is uncommonly simple and easy for practical application in comparison to well-known methods of the utilization chitosan derivatives.

The modified viscose fibres obtained in accordance with the invention are characterized by several advantages in comparison to standard viscose fibres as well as to viscose fibres containing only unmodified microcrystalline chitosan. The fibres according to the invention are characterized by a higher sorption of water and dyes, especially acid, disperse and direct type dyes. At the same time these fibres are characterized by a swelling coefficient higher than 100-120%, whereas standard viscose fibres are characterized by a value of the above parameter on a level of 60-80%, and the value of viscose fibres containing standard microcrystalline chitosan is on a level 90-120%. The modified viscose fibres obtained according to the invention can be used as super-absorbent fibres.

The modified viscose fibres containing modified microcrystalline chitosan in a form of a chelate, obtained according to the invented method, are characterized by special properties such as bacteriostaticity, when, for example, a copper chelate of microcrystalline chitosan is used. The modified viscose fibres obtained according to the invention are characterized also by bioactivity, such as for example in improving the blood coagulability.

Introduction of the modified microcrystalline chitosan to viscose fibres in accordance to the invention allows to affect their structure in dependence of the modified microcrystalline chitosan content, type of the modified polymer and the spinning parameters used. An important advantage of the invention is concerned with a high efficacy of a relatively small amount of modified microcrystalline chitosan contained in the structure the viscose fibres, whereby it may be obtained by both systems by introducing it to a viscose dope or by aftertreatment with metal ions, affecting considerably the properties of fibres obtained as for example bacteriostatic action, bioactivity, dyeability, swelling behaviour, super-molecular structure etc.

The method according to the invention allows to manufacture modified viscose fibres with special properties suitable above all for medical use, such as hospital textiles and wound bandages and dressings without difficulties in technological operations. The object is further to develop modified viscose fibres that can be used for medical, pharmaceutical, sanitary or textile applications to produce fabrics, knitwears, non-wovens and sanitary or medical cellulosic wool with special properties.

The following methods for determination of properties of the viscose fibres as well as the modified micro-crystalline chitosan have been used.:

- 5     - average molecular weight of chitosan  
          according to the method described in  
          "Chitin", Pergamon Press, New York, 1977
- 10    - deacetylation degree of chitosan  
          according to the infrared method described  
          in the International Journal of Biological  
          Macromolecules, v. 2, p. 115, 1980
- 15    - crystallinity index of viscose fibres  
          according to the infrared method described  
          in the Textile Research Journal, v. 29,  
          p. 786, 1959
- 20    - water retention value WRV  
          according to the method describe in the  
          Journal of Applied Polymer Science, v.  
          33, p. 177, 1987
- 25    - the mechanical properties of viscose fibres  
          according to the Finnish standards of  
          SFS-3984 and SFS-4639
- 30    - the swelling coefficient of viscose fibres  
          by introduction of a sample to distilled  
          water for 20 h at 20°C and by determining  
          after filtration and centrifugation for  
          80 s in 3000 r.p.m. the weight  $m_0$  and  
          after subsequent drying at a temperature  
          of 105°C by determining the weight  $m_1$ .  
35    The swelling coefficient SC was calculated  
          from equation:

$$SC = \frac{m_0 - m_1}{m_1} \cdot 100\%$$

5

- the bacteriostatic action of viscose fibres obtained determined using the Plate Count Agar method

10 A standard processes of spinning of viscose fibres and standard finishing methods were used for the manufacture of modified viscose fibres.

The invention is explained further in the following  
15 examples which do not restrict the scope of the appended claims.

#### Example 1

20 390 weight parts of microcrystalline chitosan in a water dispersion form containing 4.1 wt% of microcrystalline polymer characterized by average molecular weight of  $2.81 \cdot 10^5$ , WRV of 535%, deacetylation degree of 67.5% and nitrogen content of 7.2% was  
25 mixed for 5 minutes with 15.9 weight parts of hydrated copper sulfate dissolved in 100 weight parts of water, whereafter 5.5 weight parts of Avolan IS as a surfactant was added and the mixture was stirred for next 30 minutes. Then the modified microcrystalline chitosan  
30 was added to 5330 weight parts of viscose containing 10 wt% of  $\alpha$ -cellulose by mixing for 30 minutes. A tank containing the modified viscose was next connected with reduced pressure for removing the air-bubbles and the standard spinning process was applied to the  
35 modified viscose fibres as well as to standard viscose fibres serving as a reference.



The distribution of modified microcrystalline chitosan particles in viscose showed that the content of particles having largest dimension of 50 - 63  $\mu\text{m}$  was only 3.8%.

5

The spinning of viscose fibers was carried out with a speed of 40 m/min for a first bath containing solution of sulfuric acid in a concentration of 90 g/l and zinc sulfate of 35 g/l, for a second bath containing  
10 sulfuric acid solution in a concentration of 30 g/l at 90°C and for a third bath with the same composition at a temperature of 60°C. The fibres obtained were finished in standard conditions.

15 The modified viscose fibres obtained, containing 0.12 wt% of nitrogen responsive to 1.85 wt% of chitosan introduced into the structure and 0.66 wt% of copper were characterized by thickness of 2.90 dtex, tensile strenght of 0.82 cN/tex, elongation of 13.6%, swelling  
20 coefficient of 111.5% and crystallinity index of 45.7%.

The standard viscose fibres obtained in these same conditions were characterized by thickness of 1.74 dtex, tensile strength of 1.61 cN/dtex, elongation of  
25 19.9%, swelling coefficient of 57.9% and crystallinity index on 53.2%.

The bacteriostatic action of modified viscose fibres in a case of *Klebsiella pneumoniae* and *Escherichia coli* was very good, whereas in the standard viscose  
30 fibres this behaviour was not showed against above bacterias at all.

#### Example 2

35

390 weight parts of microcrystalline chitosan with properties as in Example 1 was mixed for 5 minutes with a solution of 11.0 weight parts of calcium

chloride and 100 weight parts of water, whereafter 5.5 weight parts of Avolan IS was added and the mixture was stirred for next 30 minutes. The modified microcrystalline chitosan was then added to 5330 weight parts of viscose containing 10 wt% of  $\alpha$ -cellulose by mixing for 30 minutes and then the modified viscose was prepared as in Example 1.

The distribution of the modified microcrystalline chitosan particles in viscose before spinning showed that the content of particles having largest dimension of 50 - 63  $\mu$ m was only 5.7%.

The spinning and finishing of modified viscose fibres was realized as in Example 1 with extension of 23%.

The modified viscose fibres obtained, containing 0.20 wt% of nitrogen respensive to 3.0 wt% of chitosan introduced to their structure and 0.02 wt% of calcium, were characterized by thickness of 2.99 dtex, tensile strength of 1.58 cN/tex, elongation of 37.2%, swelling coefficient of 111.7% and crystallinity index of 50.1%.

The bacteriostatic action of modified viscose fibres in the case of test bacteria was poor. However, these fibres were suitable as bandage material with blood coagulant behaviour.

### Example 3

390 weight parts of microcrystalline chitosan with properties as in Example 1 was mixed for 5 minutes with a solution of 17.7 weight parts of zinc sulfate and 100 weight parts of water, whereafter 5.5 weight parts of Avolan IS was added and the mixture was stirred for next 30 minutes. The modified microcrystalline chitosan was added to 5330 weight parts of viscose containing 10 wt% of  $\alpha$ -cellulose by mixing

for 10 minutes, whereafter the viscose was prepared as in Example 1.

5 The distribution of modified microcrystalline chitosan particles in viscose before spinning showed that the content of particles with largest dimension of 50-63  $\mu\text{m}$  was only 3.4%.

10 The spinning and finishing of modified viscose fibres was realized as in Example 1 with extension of 18%.

15 The modified viscose fibres, containing 0.16 wt% of nitrogen responsive to 2.7 wt% of chitosan introduced to their structure and 0.09 wt% of zinc, were characterized by thickness of 4.33 dtex, tensile strength of 1.35 cN/tex, elongation of 35.8%, swelling coefficient of 113.0% and crystallinity index of 50.8%.

20 The bacteriostatic action of modified fibres in the case of test bacteria of *Escherichia coli* was suitably good but in a case of *Klebsiella pneumoniae* was poor.

#### Example 4

25 800 weight parts of microcrystalline chitosan in a dispersion form containing 1.81 wt% of microcrystalline polymer characterized by average molecular weight of  $4.2 \cdot 10^5$ , WRV of 700%, deacetylation degree of 62% and nitrogen content of 6.9% was mixed with 2.5 weight  
30 parts of hydrated copper sulfate for 10 minutes. The modified microcrystalline chitosan was next added to 2896 weight parts of viscose containing 10 wt% of  $\alpha$ -cellulose by stirring for 1 h, then the modified viscose was prepared as in Example 1. The spinning  
35 with a speed of 23 m/min and finishing was realized as in Example 1. The modified viscose fibres, containing 0.21 wt% of nitrogen responsive to 3.0 wt% of chitosan introduced to their structure and 0.62 wt%

of copper, were characterized by tensile strength of 0.44 cN/tex, elongation of 7.6, WRV of 125% and crystallinity of 50.0%.

- 5 The bacteriostatic action of modified viscose fibres in the case of test bacteria was very good.

#### Example 5

- 10 390 weight parts of microcrystalline chitosan with properties as in Example 1 was mixed for 10 minutes with 1000 weight parts of viscose containing 10 wt% of  $\alpha$ -cellulose, whereafter this mixture was added to 4330 weight parts of the above viscose with stirring  
15 for 30 minutes, whereafter the viscose was prepared as in Example 1.

- The distribution of microcrystalline chitosan particles in the viscose before spinning showed that the content  
20 of particles with largest dimension of 50 - 63  $\mu\text{m}$  was only 4.1%.

- The spinning and finishing of modified viscose fibres was realized as in Example 1 with extension of 48%.

- 25 10 weight parts, calculated on a dry weight, of wet, undried viscose fibres containing microcrystalline chitosan was treated with stirring for 5 minutes at 20°C with 200 volume parts of water solution containing  
30 0.54 wt% of hydrated copper sulfate, whereafter the fibres were washed to remove the excess of modifying solution and subsequently dried.

- The modified viscose fibres, containing 0.18 wt% of  
35 nitrogen responsive to 2.7 wt% of chitosan introduced to their structure and 0.17 wt% of copper, were

characterized by thickness of 2.02 dtex, tensile strength of 1.93 cN/tex, elongation of 22.3%, swelling coefficient of 106% and crystallinity index of 43.4%.

- 5 The bacteriostatic action of modified viscose fibres in the case of *Escherichia coli* was excellent and in the case of *Klebsiella pneumoniae* bacteria was poor.

Example 6

10

- 650 weight parts of microcrystalline chitosan with properties as in Example 1 was mixed for 30 minutes with 5330 weight parts of viscose containing 10 wt% of  $\alpha$ -cellulose and 5.5 weight parts of Avolan IS, 15 whereafter the viscose was prepared as in Example 1.

- The distribution of microcrystalline chitosan particles in the viscose before spinning showed that the content of particles with largest dimension of 50 - 63  $\mu$ m was 20 only 2.6%.

The spinning and finishing was realized as in Example 1 with a speed of 40 m/min and extension of 40%.

- 25 10 weight parts of dry viscose fibres containing microcrystalline chitosan was treated with stirring in 200 volume parts of water solution containing 1.1 weight parts of hydrated copper sulfate as in Example 5.

30

- The modified viscose fibres, containing 0.30 wt% of nitrogen responsive to 4.6 wt% of chitosan introduced to their structure and 0.53 wt% of copper, were characterized by thickness of 2.32 dtex, tensile 35 strength of 1.76 cN/tex, elongaion of 28.5%, swelling coefficient of 11.43% and crystallinity index of 46.5%.

The bacteriostatic action of modified viscose fibres was excellent in the case of *Escherichia coli* bacteria, whereas in the case of *Klebsiella pneumoniae* it was poor.

5

#### Example 7

20 weight parts of dry viscose fibres containing microcrystalline chitosan obtained as in Example 6  
10 was treated by 200 volume parts of water solution containing 1.0 weight part of zinc sulfate for 5 minutes at 20°C using stirring as in Example 5.

15 The modified viscose fibres containing 0.26 wt% of zinc were characterized by similar properties as in Example 6. The bacteriostatic action of modified viscose fibres in the case of *Escherichia coli* bacteria was good, whereas in the case of *Klebsiella pneumoniae* bacteria it was poor.

Claims:

1. Modified viscose fibres comprising viscose cellulose and containing in their structure microcrystalline chitosan forming after spinning mainly hydrogen bonds with the regenerated cellulose of viscose fibres, characterized in that the microcrystalline chitosan contains chelated metal ions in order to modify and improve the properties of viscose fibres.
2. Viscose fibres as claimed in claim 1, characterized in that the percentage of microcrystalline chitosan is not less than 0.01 wt%, especially 0.1-20 wt%, the content of metal salts is 0.001 - 2 wt% and the content of  $\alpha$ -cellulose is 60 - 90 wt%, the remainder being water and finishing agents.
3. Viscose fibres as claimed in claim 1 or 2, characterized in that the microcrystalline chitosan used for the modification of viscose fibres, such as in the form of a dispersion preferably in water, is characterized by a water retention value within a range of 500 - 2000% in a dispersion form and 200-800% in a powder form, average molecular weight ranging from  $10^4$  to  $10^6$ , deacetylation degree not less than 30%, especially 60 - 90%, content of polymer in dispersion not less than 0.01 wt%, preferably 0.5-5.0 wt%, the chitosan being modified by chelatable metal ions such as copper, zinc or calcium, with a molar ratio of glucosamine units to metals not higher than 1:2, preferably 1:0.5 to 1:1 before introduction into a viscose dope, or in a molar ratio not less than 1:0.1 in the case of aftertreatment of viscose fibres containing microcrystalline chitosan.
4. A method of manufacture of modified viscose fibres as claimed in claim 1, characterized in that the microcrystalline chitosan is modified with the

chelatable active metal ions, such as copper, zinc or calcium, the modifying stage being carried out especially in the form of water dispersion containing not less than 0.01 wt% of the microcrystalline polymer on a dry weight, especially 0.5 - 5.0 wt%, and the ions being chelated to the glucosamine units in a molar ratio of glucosamine units to metal ions not higher than 1:2, whereafter the modified chitosan is distributed into a viscose dope, preferably by mixing for a time within a range 1 - 120 minutes or by spurting before spinning, whereafter the mixture is optionally filtered and the spinning of the modified viscose fibres is realized.

5. A method as claimed in claim 4, characterized in that the microcrystalline chitosan, especially in a water dispersion, containing not less than 0.01 wt% of polymer, is modified by the chelating active metal ions by introduction of active metal salts such as copper sulfate, zinc chloride or sulfate and calcium sulfate in a form of solid or solution, into a microcrystalline chitosan dispersion in a molar ratio of glucosamine units to metal ions not higher than 1:2, preferably 1:0.5 to 1:1, using mixing for 1 - 120 minutes at a temperature not lower than 10°C, preferably at a temperature ranging from 20° to 40°C.

6. A method as claimed in claim 4 or 5, characterized in that the introducing of microcrystalline chitosan modified by chelatable metal ions is realized by preparation of a concentrate of modified microcrystalline chitosan in viscose containing 1 - 99.9 wt% of modified microcrystalline chitosan, the remainder being viscose, using a mixing or spurting system, especially for 1 - 60 minutes, whereafter the modified microcrystalline chitosan-viscose concentrate is introduced to the viscose dope by mixing or spurting and the modified viscose fibres are produced.

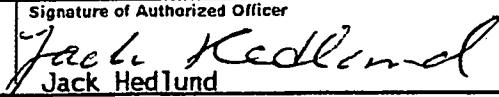
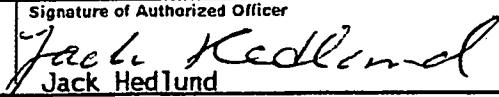
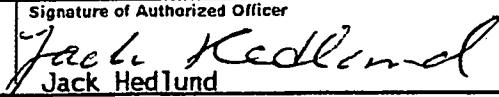


7. A method as claimed in any of claims 4 to 6, characterized in that modifying compounds, especially affecting the mixability, filtrability or  
5 improving spinning process, such as polyethylene glycols, amines, polyamines or ethoxylated phenols, in an amount not less than 0.01 wt% on a weight of  $\alpha$ -cellulose, is added to the modified microcrystalline chitosan, and/or microcrystalline chitosan-viscose  
10 concentrate and/or viscose and/or to the modified viscose.

8. A method of manufacture of modified viscose fibres as claimed in claim 1, characterized in  
15 that the viscose fibres obtained after spinning and containing microcrystalline chitosan are subjected to an aftertreatment using a solution of chelatable metal ions, such as copper, zinc or calcium, in a form of copper sulfate, zinc chloride or sulfate or calcium  
20 chloride for example, in a molar ratio of glucosamine units to metal ions not lower than 1:0.1, preferably 1:0.5 to 1:2, by mixing, washing or dipping of modified viscose fibres for a time ranging from 1 to 120 minutes at a temperature not lower than 10°C, especially 20-  
25 60°C.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/FI 90/00292

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: D 01 F 2/08, 11/02																	
<b>II. FIELDS SEARCHED</b> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched<sup>7</sup></div> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 25%; border-bottom: 1px solid black;">Classification System</td> <td style="border-bottom: 1px solid black;">Classification Symbols</td> </tr> <tr> <td style="height: 40px; vertical-align: bottom;">IPC5</td> <td style="vertical-align: bottom;">D 01 F</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched<sup>8</sup></div> <p>SE,DK,FI,NO classes as above</p>			Classification System	Classification Symbols	IPC5	D 01 F											
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<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category *</th> <th style="width: 60%;">Citation of Document,<sup>11</sup> with indication, where appropriate, of the relevant passages<sup>12</sup></th> <th style="width: 30%;">Relevant to Claim No.<sup>13</sup></th> </tr> </thead> <tbody> <tr> <td style="text-align: center;">A</td> <td>WO, A1, 8801316 (FIREXTRA OY) 25 February 1988, see the whole document --</td> <td style="text-align: center;">1-8</td> </tr> <tr> <td style="text-align: center;">A</td> <td>FI, B, 78126 (VALTION TEKNILLINEN TUTKIMUSKESKUS) 28 February 1989, see the whole document --</td> <td style="text-align: center;">1-8</td> </tr> <tr> <td style="text-align: center;">A</td> <td>FI, B, 78127 (VALTION TEKNILLINEN TUTKIMUSKESKUS) 28 February 1989, see the whole document --</td> <td style="text-align: center;">1-8</td> </tr> <tr> <td style="text-align: center;">A</td> <td>Chemical Abstracts, volume 102, no. 2, 14 January 1985, (Columbus, Ohio, US), see page 367, abstract 12433f, &amp; JP, 59116418 (Fuji Spinning Co., Ltd.) 1984 --</td> <td style="text-align: center;">1-8</td> </tr> </tbody> </table>			Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>	A	WO, A1, 8801316 (FIREXTRA OY) 25 February 1988, see the whole document --	1-8	A	FI, B, 78126 (VALTION TEKNILLINEN TUTKIMUSKESKUS) 28 February 1989, see the whole document --	1-8	A	FI, B, 78127 (VALTION TEKNILLINEN TUTKIMUSKESKUS) 28 February 1989, see the whole document --	1-8	A	Chemical Abstracts, volume 102, no. 2, 14 January 1985, (Columbus, Ohio, US), see page 367, abstract 12433f, & JP, 59116418 (Fuji Spinning Co., Ltd.) 1984 --	1-8
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents:<sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>																	
<b>IV. CERTIFICATION</b> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black;">Date of the Actual Completion of the International Search</td> <td style="width: 50%; border-bottom: 1px solid black;">Date of Mailing of this International Search Report</td> </tr> <tr> <td style="text-align: center;">8th March 1991</td> <td style="text-align: center;">1991 -03- 13</td> </tr> <tr> <td style="border-bottom: 1px solid black;">International Searching Authority</td> <td style="border-bottom: 1px solid black;">Signature of Authorized Officer</td> </tr> <tr> <td style="text-align: center;">SWEDISH PATENT OFFICE</td> <td style="text-align: center;">             Jack Hedlund         </td> </tr> </table>			Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	8th March 1991	1991 -03- 13	International Searching Authority	Signature of Authorized Officer	SWEDISH PATENT OFFICE	 Jack Hedlund							
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
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A	<p>Chemical Abstracts, volume 102, no. 23, 10 June 1985, (Columbus, Ohio, US), Ogawa, Kozo et al: "X-ray diffraction study on chitosan-metal complexes ", see page 625, abstract 204210c, &amp; Chitin, Chitosan, Relat. Enzymes 1984,, 327-345ä</p> <p>-----</p>	1-8

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.PCT/FI 90/00292**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the Swedish Patent Office EDP file on **91-01-31**  
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A1- 8801316	88-02-25	EP-A- 0319536	89-06-14
FI-B- 78126	89-02-28	NONE	
FI-B- 78127	89-02-28	NONE	